DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to organic electroluminescence devices and a blue light element, and relates to the thin film type device which emits light applying an electric field to the luminous layer which comprises an organic compound in detail.
[0002]
[Description of the Prior Art]Although what doped Mn which is a luminescence center, and rare earth elements (Eu, Ce, Tb, Sm, etc.) is common to ZnS and CaS which are II-VI group compound semiconductors of an inorganic material, SrS, etc. as a thin film type electroluminescence (EL) element conventionally, The EL element produced from the above-mentioned inorganic material has the problem that one alternating current drive is [necessity (50-1000 Hz) and 2 driver voltage] high (-200V) and that the formation of 3 full color has the high cost of difficulty (especially blue) and 4 circumference drive circuit.
[0003]However, development of the EL element using an organic thin film came to be performed in recent years for improvement of the above-mentioned problem. In order to raise luminous efficiency especially, the kind of electrode is optimized for the purpose of the improve efficiency of carrier pouring from an electrode, By development (Appl. Phys. Lett., 51 volumes, 913 pages, 1987) of the organic electroluminescence devices which provided the electron hole transporting bed which comprises aromatic diamine, and the luminous layer which comprises the aluminium complex of 8-hydroxyquinoline. The extensive improvement of luminous efficiency is made as compared with the EL element using single crystals, such as the conventional anthracene. By what fluorochromes for laser, such as a coumarin, are doped for by using the aluminium complex of 8-hydroxyquinoline as a host material, for example (J. Appl.Phys., 65 volumes, 3610 pages, 1989). Improvement in luminous efficiency, conversion of the luminous wavelength, etc. are performed, and the practical use characteristic is

approached.

[0004]Besides the electroluminescence devices using the above low molecule materials, as a material of a luminous layer, Poly (p-phenylenevinylene), poly [2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene], Development of the electroluminescence devices using polymer materials, such as poly (3-alkyl thiophene), and development of the element which mixed a low-molecular luminescent material and electronic transition material to polymers, such as a polyvinyl carbazole, are also performed.

[0005]Improvement in driving stability is mentioned as one of the big technical problems at the time of applying organic electroluminescence devices to the field of a flat panel display. In the organic electroluminescence devices which make it come to laminate especially low molecule material, that the life of a blue element is short as compared with other luminescent color poses a problem. The blue light element is required for a white light element besides the dot-matrix type full color display device which needs blue as the luminescent color, and the reinforcement has been an indispensable technical problem in utilization.

[0006]In respect of the application to a small character representation element, a simple-matrix-driving method is mainly adopted. In this method, in order to make an element emit light extremely by a high duty ratio for a short time, although it is advantageous, it is necessary to make light emit with high-intensity dramatically, therefore there is a problem that life decline is promoted, to the heat generated for an element.

[0007]In the organic electroluminescence devices reported until now, luminescence has been fundamentally obtained with the combination of an electron hole transporting bed and an electron transport layer. In this element, it is a principle to recombine the electron hole poured in from the anode with the electron which moves an electron hole transporting bed, is poured in from the negative pole, and moves an electron transport layer near the interface of both layers, to excite an electron hole transporting bed and/or an electron transport layer, and to make light emit. By providing a luminous layer between an electron hole transporting bed and an electron transport layer in recent years, the element which is raising luminous efficiency is common.

[0008]Exciton generation in a luminous layer may be promoted and a hole blocking layer may be provided between a luminous layer and an electron transport layer for the purpose of efficient-izing of luminescence, and high-grade-izing of the luminescent color. In particular, with a blue light element, it is general. About these hole blocking layers as a hole blocking layer which has ionization potential bigger 0.1 eV or more than the ionization potential of a luminous layer established between a luminous layer and the negative pole, Driving stability was not enough although the element which provided tris(5,7-dichloro 8-hydroxy KINORINO) aluminum (JP,2-195683,A) and the hole blocking layer which consists of silacyclo pentadiene (the No. publication-number 9- 87616 gazette) was proposed. The electrochemical factor etc. to which

material will return and oxidize by pouring of the heat deterioration, electron, and electron hole which originate in the glass transition temperature (Tg) of material being low as a factor of this drive degradation are considered.

[0009]In organic electroluminescence devices, in order to produce high luminous efficiency and a stable element, it is required to convey efficiently the electron poured in from the negative pole to a luminous layer and to prevent the electron hole which passes a luminous layer, and the further improvement examination was desired to the element structure and material for it.

[0010]Although organic electroluminescence devices using the layer containing 4,4'-JI (N-carbazolyl) biphenyl as a negative pole volume phase are indicated to JP,8-60144,A, Having the electron hole checking action excellent in the compound of the specific structure which has N-phenyl carbazole group is not indicated at all.

[0011]

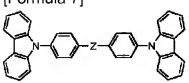
[Problem(s) to be Solved by the Invention]This invention can convey efficiently the electron poured in from the negative pole to a luminous layer, Can prevent certainly the electron hole which passes a luminous layer, and it has the hole blocking layer which was moreover excellent also in heat-resistant degradation or electrochemical stability, Therefore, it is possible to emit light efficient with high color purity in the target luminescent color, and also it aims at providing organic electroluminescence devices and a blue light element excellent also in driving stability.

[0012]

[Means for Solving the Problem]Organic electroluminescence devices of this invention have on a substrate the luminous layer pinched by the anode and the negative pole, and this hole blocking layer contains a compound expressed with following general formula (I) in organic electroluminescence devices in which a hole blocking layer was provided in contact with an interface by the side of this negative pole of this luminous layer.

[0013]

[Formula 7]



(I)

[0014](Among a formula, it may have arbitrary substituents, and these substituents may join together, and the carbazolyl group and the phenylene group may form the ring condensed in a carbazolyl group or a phenylene group.) Z shows a divalent connecting group.

[0015]A blue light element of this invention consists of organic electroluminescence devices of such this invention.

[0016]That is, as a result of inquiring wholeheartedly that the above-mentioned purpose should be attained, this invention persons find out that the purpose of this invention can be attained by using the above-mentioned specific compound as a material of a hole blocking layer, and came to complete this invention.

[0017]A blue light element of this invention consists of organic electroluminescence devices of such this invention.

[0018]Ionization potential of a substance which contributes material which constitutes a hole blocking layer to luminescence in a luminous layer (when a luminous layer contains a host material and a dopant so that it may mention later) It is preferred to have ionization potential bigger 0.1 eV or more than ionization potential of a host material. It is required to be a compound which gives stable thin film shape, has a high glass transition temperature (Tg), and can convey an electron efficiently. It is required that an impurity which is still more nearly electrochemically and chemically stable, and serves as a trap, or quenches luminescence should be a compound which is hard to generate at the time of manufacture and use.

[0019]If it is a compound which has N-phenyl carbazole skeleton expressed with said general formula (I), It is possible to fill all such demand specification, therefore to emit light efficient with high color purity in the target luminescent color, and also organic electroluminescence devices excellent also in driving stability can be realized.

[0020]

[Embodiment of the Invention]Below, the embodiment of the organic electroluminescence devices of this invention and a blue light element is described in detail.

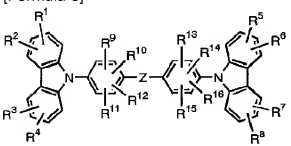
[0021]First, in the organic electroluminescence devices of this invention, the compound expressed with said general formula (I) which constitutes a hole blocking layer is explained.

[0022]Although the compound expressed with said general formula (I) may have arbitrary substituents on the carbazolyl group and/or a phenylene group, as long as it does not have an adverse effect on the basic characteristic of this invention, as the substituent, what kind of substituent may be sufficient as it. The ring may be formed by these substituents.

[0023]The compound expressed with said general formula (I) is preferably expressed with a following general formula (I').

[0024]

[Formula 8]



(I ')

[0025](I') the inside of a formula, R^1 - R^{16} -- each -- independent -- a hydrogen atom. A halogen atom, an alkyl group, an aralkyl group, an alkenyl group, a cyano group, An amino group, an acyl group, an alkoxycarbonyl group, a carboxyl group, an alkoxy group, An alkylamino group, an aralkyl amino group, a halo alkyl group, a hydroxyl group, The aromatic-hydrocarbon-rings group or aromatic heterocycle group which may have an aryloxy group and a substituent is expressed, R^1, R^2 and R^3, R^4 and R^5, and R^6, R^7, R^8 and R^9, R^{10} and R^{11}, R^{12} and R^{13}, R^{14} and R^{15}, and R^{16} may form a ring unitedly, respectively. Z shows a divalent connecting group.

[0026](I') As R^1 in a formula - R^{16}, specifically A hydrogen atom; chlorine atom, Halogen atoms, such as a fluorine atom; An alkenyl group; cyano group; amino group; acyl group; methoxycarbonyl group of the carbon numbers 2-6, such as aralkyl group; vinyl groups, such as alkyl group; benzyl of the carbon numbers 1-6, such as a methyl group and an ethyl group, alkoxycarbonyl group [of the carbon numbers 2-6 of an ethoxycarbonyl group etc.]; -- carboxyl group; -- a methoxy group. An alkoxy group of the carbon numbers 1-6, such as an ethoxy basis; Dialkylamino group; dibenzylamino groups, such as a diethylamino group and a diisopropylamino group, diaralkylamino group [, such as a diphenethyl amino group,]; -- alpha-halo alkyl group [, such as a trifluoromethyl group,]; -- hydroxyl group; -- a phenoxy group. Aryloxy groups, such as a benzyloxy group; aromatic heterocycle groups which may have aromatic-hydrocarbon-rings group; substituents, such as a phenyl group, a naphthyl group, etc. which may have a substituent, such as a thienyl group and a pyridyl group, are mentioned.

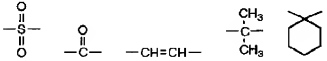
[0027]As a substituent which said aromatic-hydrocarbon-rings group and an aromatic heterocycle group may have, Halogen atoms, such as a fluorine atom; An alkenyl group; methoxycarbonyl group of the carbon numbers 2-6, such as an alkyl group; vinyl group of the carbon numbers 1-6, such as a methyl group and an ethyl group, An alkoxycarbonyl group of the carbon numbers 2-6 of an ethoxycarbonyl group etc.; A methoxy group, An alkoxy group of the carbon numbers 1-6, such as an ethoxy basis; halo alkyl group; cyano groups, such as acyl group; trifluoromethyl groups, such as alkylamino group; acetyl groups, such as aryloxy group; dimethylamino groups, such as a phenoxy group and a benzyloxy group, and a diethylamino group, etc. are mentioned.

[0028]R^1, R^2 and R^3, and R^4, R^5, R^6 and R^7, R^8 and R^9, and R^{10}, It may join together and R^{11}, R^{12} and R^{13}, R^{14} and R^{15}, and R^{16} may form five to 7 membered-rings, such as the benzene ring and a cyclohexane ring, respectively.

[0029]Especially a desirable thing is a hydrogen atom, an alkyl group, or a cyano group as R^1

thru/or R^{16}.

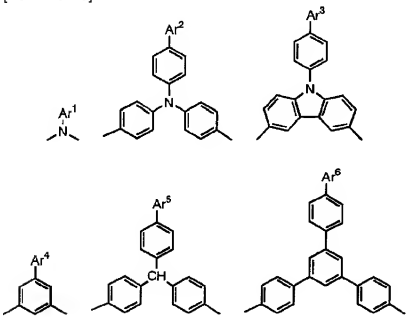
[0030]A connecting group preferably shown below as Z in general formula (I) or (I'), [Formula 9]



Either the divalent aromatic-hydrocarbon-rings group or aromatic heterocycle group which may have a substituent, or the following connecting groups are mentioned.

[0031]

[Formula 10]



[0032](Each benzene ring portion in the above-mentioned structure may have arbitrary substituents, and an aromatic-hydrocarbon-rings group with which Ar^1 - Ar^6 may have a substituent, an aromatic heterocycle group, or a basis expressed with general formula (II) of the following is mentioned.)

[Formula 11]

(II)

formula (II) -- an inner carbazolyl group and phenylene group may have arbitrary substituents.

[0033]As general formula (I) or an aromatic-hydrocarbon-rings group of Z in (I'), the monocycle of 5 or 6 membered-rings, such as a phenylene group, a naphthylene group, an anthracene

group, and a naphthacene group, or 2 - 4 condensed ring is mentioned, for example. As an aromatic heterocycle group of Z, the monocycle of 5 or 6 membered-rings or two to 3 condensed rings, such as a thiophene group, a franc group, a pyridine group, a pyrimidine group, and a quinoline group, are mentioned, for example.

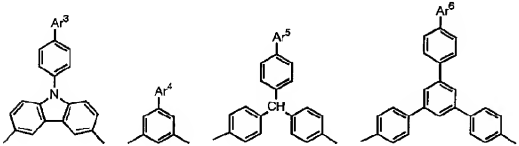
[0034]Each of these aromatic-hydrocarbon-rings groups and aromatic heterocycle groups may have a substituent, and as this substituent, For example, alpha-halo alkyl group of the carbon numbers 1-6, such as halogen atoms, such as an alkyl group of the carbon numbers 1-6, such as a methyl group and an ethyl group, and a fluorine atom, and a trifluoromethyl group, etc. are mentioned.

[0035]As Ar^1 - Ar^6, a phenyl group, a naphthyl group, An aromatic heterocycle group which is a monocycle of 5 or 6 membered-rings, such as an aromatic-hydrocarbon-rings group which is a monocycle of 5 or 6 membered-rings, such as an anthranil and a naphthacene group, or two to 4 condensed ring, a thienyl group, a furil group, a pyridyl group, a pyrimidyl group, and a quinolyl group, or two to 3 condensed ring is mentioned. Each of these may have substituents, such as alpha-halo alkyl group of the carbon numbers 1-6, such as halogen atoms, such as an alkyl group of the carbon numbers 1-6, such as a methyl group and an ethyl group, and a fluorine atom, and a trifluoromethyl group.

[0036]As for general formula (I) or Z in (I'), it is still more preferred that they are either [which may have a substituent from a viewpoint of electron hole inhibition nature] a phenylene group, a naphthylene group, an anthracene group, a thiophene group, a franc group or the following connecting groups.

[0037]

[Formula 12]



[0038](The aromatic-hydrocarbon-rings group with which each benzene ring portion in each above-mentioned structure may have arbitrary substituents, and Ar^3 - Ar^6 may have a substituent, an aromatic heterocycle group, or formula (II) shown below)

[Formula 13]

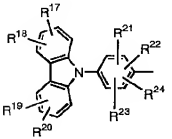
(II)

It comes out and is either of the bases which is expressed. The carbazolyl group and phenylene group in formula (II) Naka may have arbitrary substituents.

[0039]The structure expressed with formula (II) is preferably expressed with a following formula (II').

[0040]

[Formula 14]



(II')

[0041]((II') Respectively R^{17} - R^{24} independently among a formula) A hydrogen atom, a halogen atom, an alkyl group, an aralkyl group, an alkenyl group, The amino group, acyl group, alkoxycarbonyl group which may have a cyano group and a substituent, A carboxyl group, an alkoxy group, an alkylamino group, an aralkyl amino group, The aromatic-hydrocarbon-rings group or aromatic heterocycle group which may have a halo alkyl group, a hydroxyl group, an aryloxy group, and a substituent is expressed, R^{17}, R^{18} and R^{19}, R^{20} and R^{21}, R^{22} and R^{23}, and R^{24} may form a ring by adjoining substituents, respectively.

[0042]In the above-mentioned (II') formula, as R^{17} - R^{24}, specifically, hydrogen atom; -- halogen atom; -- the alkenyl group; cyano group; amino group; acyl group; methoxycarbonyl group of the carbon numbers 2-6, such as aralkyl group; vinyl groups, such as alkyl group; benzyl of the carbon numbers 1-6, such as a methyl group and an ethyl group,. alkoxycarbonyl group [of the carbon numbers 2-6 of an ethoxycarbonyl group etc.]; -- carboxyl group; -- a methoxy group. The alkoxy group of the carbon numbers 1-6, such as an ethoxy basis; Dialkylamino group; dibenzylamino groups, such as a diethylamino group and a diisopropylamino group, diaralkylamino group [, such as a diphenethyl amino group,]; -- alpha-halo alkyl group [, such as a trifluoromethyl group,]; -- hydroxyl group; -- a phenoxy group. Aryloxy groups, such as a benzyloxy group; aromatic heterocycle groups which may have aromatic-hydrocarbon-rings group; substituents, such as a phenyl group, a naphthyl group, etc. which may have a substituent, such as a thienyl group and a pyridyl group, are mentioned.

[0043]As a substituent which said aromatic-hydrocarbon-rings group and an aromatic heterocycle group may have, Halogen atoms, such as a fluorine atom; An alkenyl group;

methoxycarbonyl group of the carbon numbers 2-6, such as an alkyl group; vinyl group of the carbon numbers 1-6, such as a methyl group and an ethyl group, An alkoxycarbonyl group of the carbon numbers 2-6 of an ethoxycarbonyl group etc.; A methoxy group, An alkoxy group of the carbon numbers 1-6, such as an ethoxy basis; halo alkyl group; cyano groups, such as acyl group; trifluoromethyl groups, such as dialkylamino groups, such as aryloxy group; dimethylamino groups, such as a phenoxy group and a benzyloxy group, and a diethylamino group, and an acetyl group, etc. are mentioned.

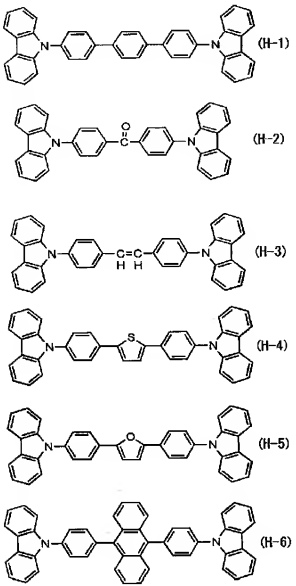
[0044]It may join together and R^{17}, R^{18} and R^{19}, R^{20} and R^{21}, R^{22} and R^{23}, and R^{24} may form five to 7 membered-rings, such as the benzene ring and a cyclohexane ring, respectively.

[0045]Especially a desirable thing is a hydrogen atom, an alkyl group, or a cyano group as R^{17} thru/or R^{24}.

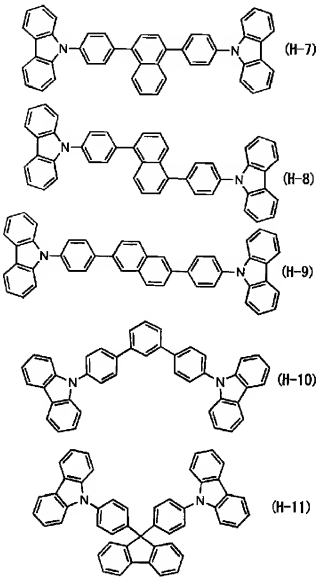
[0046]Although a desirable example of a compound expressed with said general formula (I) is shown below, it does not limit to these.

[0047]

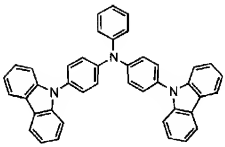
[Formula 15]



[0048]
[Formula 16]



[0049]
[Formula 17]



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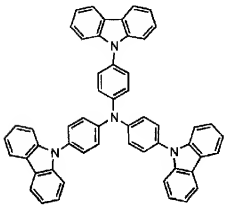

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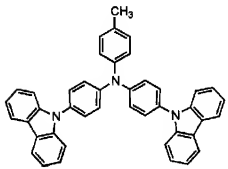

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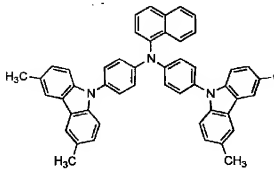
[0050]
[Formula 18]



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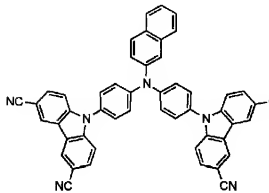

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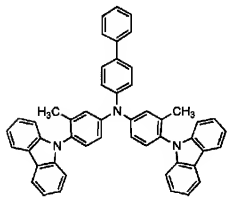
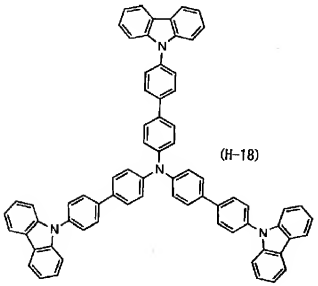


(H-17)

[0051]
[Formula 19]



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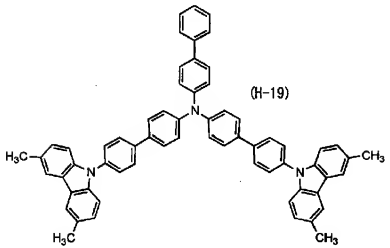

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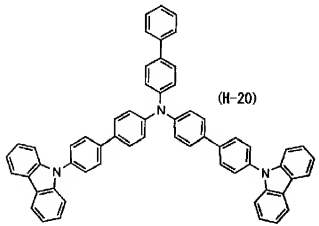
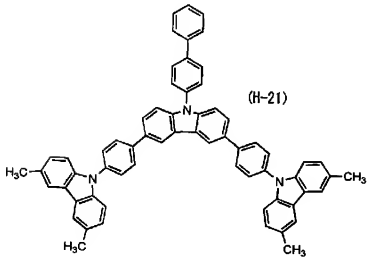
[0052]
[Formula 20]





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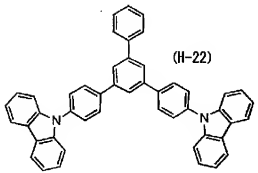
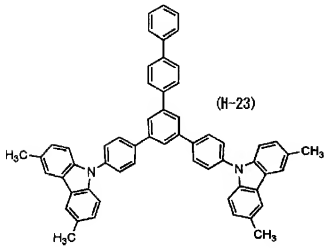
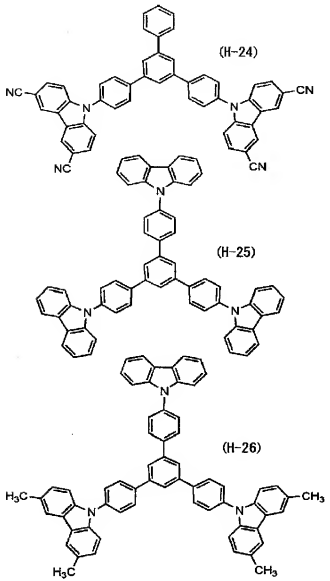




[0054]
[Formula 22]



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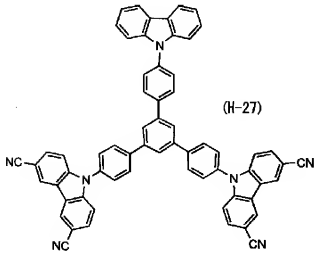

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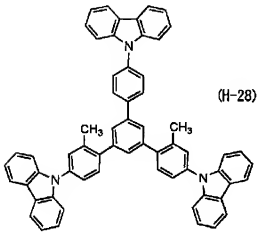
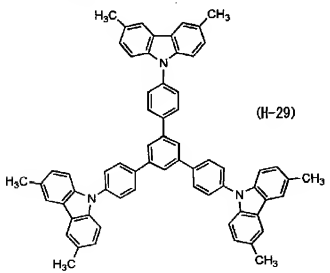


(H-28)

[0056]

[Formula 24]



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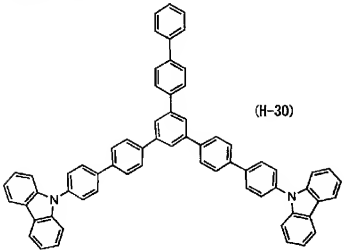
[0057]

[Formula 25]



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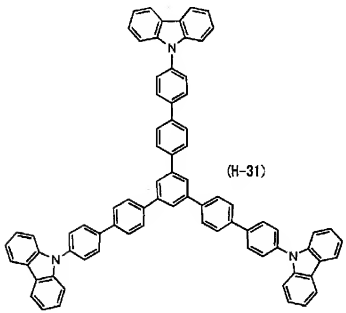
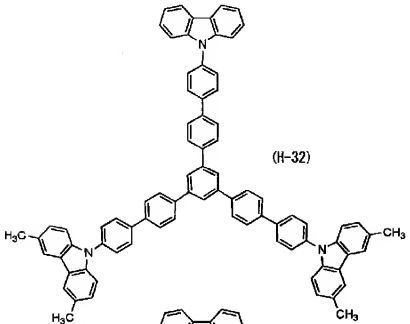
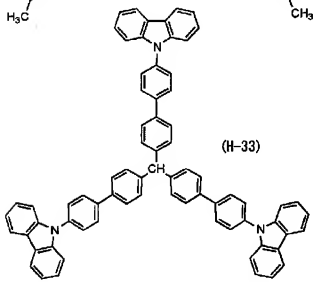


(H-31)

[0058]
[Formula 26]





[0059]Hereafter, the structure of the organic electroluminescence devices of this invention is explained, referring to drawings.

[0060]drawing 1 - 3 are the sectional views showing the embodiment of the organic electroluminescence devices of this invention typically -- 1 -- a substrate and 2 -- the anode and 3 -- a luminous layer and 6 express a hole blocking layer, 7 expresses an electron transport layer, and, as for an anode buffer layer and 4, 8 expresses the negative pole respectively, as for an electron hole transporting bed and 5.

[0061]The substrate 1 serves as a base material of organic electroluminescence devices, and the board of quartz or glass, a metal plate, a metallic foil and a plastic film, a sheet, etc. are used. The board of transparent synthetic resins, such as a glass plate, polyester, polymethacrylate, polycarbonate, polysulfone, is especially preferred. To use a synthetic resin base, it is necessary to care about gas barrier property. Since organic electroluminescence

devices may deteriorate by the open air which passed the substrate when the gas barrier property of a substrate is too small, it is not desirable. For this reason, the method of providing precise silicon oxide etc. at least in one side of a synthetic resin base, and securing gas barrier property is also one of the desirable methods.

[0062]The anode 2 is formed on the substrate 1. The anode 2 plays a role of a hole injection to the electron hole transporting bed 4. This anode 2 usually Aluminum, gold, silver, nickel, palladium, It is constituted by conductive polymers, such as halogenation metal, such as metallic oxides, such as an oxide of metal, such as platinum, indium, and/or tin, and copper iodide, carbon black or poly (3-methylthiophene), polypyrrole, and poly aniline, etc. Formation of the anode 2 is usually performed by sputtering process, a vacuum deposition method, etc. in many cases. When using particles, such as metal particles, such as silver, and copper iodide, carbon black, a conductive metal oxide particle, conductive polymer impalpable powder, etc., the anode 2 can also be formed by distributing in a suitable binder resin solution and applying on the substrate 1. A thin film can be directly formed on the substrate 1 by electrolytic polymerization, or on the substrate 1, in the case of a conductive polymer, a conductive polymer can be applied, and it can also form the anode 2 (Appl.Phys.Lett., 60 volumes, 2711 pages, 1992).

[0063]The anode 2 may be the laminated structure which laminated a layer which consists of a different material and was formed.

[0064]Thickness of the anode 2 changes with transparency to need. When transparency is needed, it is desirable to usually make transmissivity of visible light into not less than 80% preferably not less than 60%, and 5-1000 nm of thickness is usually about 10-500 nm preferably in this case. When it may be opaque, thickness of the anode 2 may be comparable as the substrate 1. It is also possible to laminate a different electrical conducting material on the above-mentioned anode 2.

[0065]The electron hole transporting bed 4 is formed on the anode 2. As conditions required of material of the electron hole transporting bed 4, hole-injection efficiency from the anode 2 is high, and it is mentioned that it is the material which can convey a poured-in electron hole efficiently. For that purpose, ionization potential is small, from light of visible light, transparency is high, hole mobility is large, it excels in stability further, and, moreover, it is required that it should be hard to generate an impurity used as a trap at the time of manufacture and use. Quenching luminescence from the luminous layer 5, in order to touch the luminous layer 5, or forming exciplex between the luminous layers 5 and not reducing efficiency is called for. Since heat resistance is further required of an element when application for a mounted display is considered in addition to the above-mentioned general demand, material which has a value of not less than 85 ** as Tg is desirable.

[0066]Aromatic diamine which two or more fused aromatic rings replaced by a nitrogen atom

as such a hole transporting material including two or more tertiary amine represented with 4,4'-bis[N-(1-naphthyl)-N-phenylamino] biphenyl, for example (JP,5-234681,A), 4,4',4" -- an aromatic amine compound (J. Lumin. -- 72 to 74 volumes) which has starburst structures, such as - tris(1-naphthyl phenylamino) triphenylamine an aromatic amine compound (Chem.Commun. -- 2175 pages) which will comprise a tetramer of a triphenylamine in 985 pages and 1997 Spiro compounds (Synth. Metals, 91 volumes, 209 pages, 1997), such as a 2,2',7,7'-tetrakis (diphenylamino)-9,9'-spirobifluorene, etc. will be mentioned in 1996. These compounds may be used independently, and if needed, it may mix respectively and they may be used.

[0067]In addition to the above-mentioned compound, as a material of the electron hole transporting bed 4, a polyvinyl carbazole, Polymer materials, such as polyarylene ether SARUHON (Polym. Adv. Tech., seven volumes, 33 pages, 1996) containing a polyvinyl triphenylamine (the No. publication-number 7- 53953 gazette) and tetraphenylbenzidine, are also mentioned.

[0068]When forming the electron hole transporting bed 4 by the applying method, to one sort of a hole transporting material, or two sorts or more. Additive agents which do not become a hole trap as occasion demands, such as binder resin and a spreading nature improving agent, are added, it dissolves, a coating solution is prepared, and it applies on the anode 2 by methods, such as a spin coat method, and it dries and the electron hole transporting bed 4 is formed. Polycarbonate, polyarylate, polyester, etc. are mentioned as binder resin. Since it will reduce hole mobility if binder resin has many additions, few directions are desirable and its 50 or less % of the weight is usually preferred at content in the electron hole transporting bed 4.

[0069]In forming the electron hole transporting bed 4 with a vacuum deposition method, After paying a hole transporting material to a crucible installed in a vacuum housing and exhausting inside of a vacuum housing even to a 10^{-4}Pa grade with a suitable vacuum pump, the electron hole transporting bed 4 is made to form on the substrate 1 which a crucible is heated and a hole transporting material was evaporated, and faced a crucible and was placed and with which the anode 2 was formed.

[0070]thickness of the electron hole transporting bed 4 -- usually -- 5-300 nm -- desirable -- It is 10-100 nm. Thus, in order to form a thin film uniformly, generally a vacuum deposition method is used well.

[0071]The luminous layer 5 is formed on the electron hole transporting bed 4. In inter-electrode [which was able to give an electric field], the luminous layer 5 is formed from a fluorescent compound in which it is excited by recombination of an electron hole which is poured in from the anode 2 and moves the electron hole transporting bed 4, and an electron which is poured in from the negative pole 8 and moves the hole blocking layer 6, and strong luminescence is shown.

[0072]It is required to be a compound which has stable thin film shape as a fluorescent compound used for the luminous layer 5, can show a high fluorescence yield according to a solid state, and can convey an electron hole and/or an electron efficiently. It is still more nearly electrochemically and chemically stable, and it is required that an impurity used as a trap should be a compound which is hard to generate at the time of manufacture and use.
[0073]As a material which fulfills such conditions, metal complexes, such as an aluminium complex of 8-hydroxyquinoline (JP,59-194393,A), A metal complex of 10-hydroxybenzo[h] quinoline (JP,6-322362,A), A screw styryl benzene derivative (JP,1-245087,A, 2-222484 gazette), A screw styryl arylene derivative (JP,2-247278,A), a metal complex (JP,8-315983,A) of benzothiazole (2-hydroxyphenyl), a silole derivative, etc. are mentioned. An aromatic amine system compound which has fluorescence among the above-mentioned electron hole transporting bed materials can also be used as a luminous layer material.
[0074]Such luminous layer materials are usually laminated on an electron hole transporting bed by a vacuum deposition method, and the luminous layer 5 is formed.
[0075]thickness of the luminous layer 5 -- usually -- 3 - 200 nm -- it is 5 - 100 nm preferably.
[0076]Although a luminous layer can also be formed by the same method as an electron hole transporting bed, a vacuum deposition method is usually used.
[0077]While raising luminous efficiency of an element, are the purpose of changing the luminescent color, and an aluminium complex of 8-hydroxyquinoline is used as a host material, for example, Doping fluorochromes for laser, such as a coumarin (J. Appl. Phys., 65 volumes, 3610 pages, and 1989) etc. is performed. This doping technique can be applied also to the luminous layer 5, and various kinds of fluorochromes can be used for it as a charge of dope material in this case besides a coumarin. As a fluorochrome which gives blue light, perylene, pyrene, anthracene, coumarins, those derivatives, etc. are mentioned. A quinacridone derivative, a coumarin derivative, etc. are mentioned as green fluorescence coloring matter. Rubrene, a peri MIDON derivative, etc. are mentioned as a yellow fluorochrome. As a red fluorochrome, a DCM system compound, a benzopyran derivative, a rhodamine derivative, a benzo thioxanthene derivative, azabenzthioxanthene, etc. are mentioned.
[0078]responding to a host material besides the above-mentioned fluorochrome for a dope -- laser research, eight volumes, 694 pages, 803 pages, and 958page(1980); -- said 9 volume and a fluorochrome currently enumerated without 85 pages (1981) can use it as a dope material for luminous layers.
[0079]As for quantity by which the above-mentioned fluorochrome is doped to a host material, 10^{-3}-10 % of the weight is preferred.
[0080]How to dope an above-mentioned fluorochrome to a host material of a luminous layer is explained below.
[0081]When forming a luminous layer by the applying method, said luminous layer host

material and a fluorochrome for a dope, Additive agents, such as binder resin which furthermore serves as neither an electronic trap nor a quencher of luminescence as occasion demands, and spreading nature improving agents, such as a leveling agent, are added, a dissolved coating solution is prepared, and it applies on the electron hole transporting bed 4 by methods, such as a spin coat method, and it dries and the luminous layer 5 is formed. Polycarbonate, polyarylate, polyester, etc. are mentioned as binder resin here. Since it will reduce an electron hole/electron mobility if binder resin has many additions, few directions are desirable and its 50 or less % of the weight is preferred at content in the luminous layer 5.

[0082]In forming a luminous layer with a vacuum deposition method, it pays said host material to a crucible installed in a vacuum housing, After putting a fluorochrome to dope into another crucible and exhausting inside of a vacuum housing even to a 10^{-4}Pa grade with a suitable vacuum pump, each crucible is heated simultaneously, and is evaporated and a layer is formed on the electron hole transporting bed 4 of a substrate placed by facing a crucible. What mixed the above-mentioned material by a predetermined ratio beforehand as other methods may be put into the same crucible, and may be evaporated.

[0083]When each above-mentioned dopant is doped in the luminous layer 5, in a thickness direction of the luminous layer 5, it is usually doped uniformly, but there may be concentration distribution in a thickness direction. For example, it may dope only near the interface with the electron hole transporting bed 4, or may dope only near the interface with the hole blocking layer 6 conversely.

[0084]The hole blocking layer 6 is laminated so that an interface by the side of the negative pole of the luminous layer 5 may be touched on the luminous layer 5. The hole blocking layer 6 is formed from a compound which can convey efficiently a role which prevents that an electron hole where it moves from the electron hole transporting bed 4 reaches the negative pole 8, and an electron poured in from the negative pole 8 in the direction of the luminous layer 5. It is needed that electron mobility is high and hole mobility is low as physical properties for which material which constitutes the hole blocking layer 6 is asked. The hole blocking layer 6 shuts up an electron hole and an electron in the luminous layer 5, and it has a function which raises luminous efficiency, therefore it is desired for ionization potential of the hole blocking layer 6 to be larger than ionization potential of the luminous layer 5 0.1 eV or more.

[0085]Although a compound expressed with said general formula (I) is used as a material of the hole blocking layer 6 in this invention, into the hole blocking layer 6, these compounds may use one sort independently, and if needed, may mix two or more sorts and may use it. Although it is desirable to comprise only a compound expressed with said general formula (I) as for a hole blocking layer, it may contain substances other than a compound expressed with said general formula (I). in this case, it being preferred that content of a compound expressed with said general formula (I) in the hole blocking layer 6 is 50 % of the weight or more, and,

when acquiring an effect of this invention certainly, It is more preferred that it is 80 % of the weight or more, and a case where it is formed only from a compound substantially expressed with general formula (I) is the most preferred.

[0086]0.3-100 nm of thickness of the hole blocking layer 6 is usually 0.5-50 nm preferably.

[0087]Although the hole blocking layer 6 can also be formed by the same method as the electron hole transporting bed 4, a vacuum deposition method is usually used.

[0088]The negative pole 8 plays a role which pours an electron into the luminous layer 5 via the hole blocking layer 6. Although the material used as the negative pole 8 can use material used for said anode 2, In order to perform electron injection efficiently, low metal of a work function is preferred and suitable metal or those alloys, such as tin, magnesium, indium, calcium, aluminum, and silver, are used. As an example, low work function alloy electrodes, such as a magnesium silver alloy, a magnesium indium alloy, and an aluminium-lithium alloy, are mentioned.

[0089]Thickness of the negative pole 8 is usually the same as that of the anode 2.

[0090]When increasing the stability of an element, it is preferred that a work function laminates a stable metal layer to the atmosphere further highly on this, in order to protect the negative pole which comprises a low work function metal. For this purpose, metal, such as aluminum, silver, copper, nickel, chromium, gold, and platinum, is used.

[0091]As shown in drawing 2 for the purpose of raising luminous efficiency of an element further, it is possible to form the electron transport layer 7 between the hole blocking layer 6 and the negative pole 8. The electron transport layer 7 is formed from a compound which can convey efficiently an electron poured in from the negative pole 8 in inter-electrode [which was able to give an electric field] in the direction of the hole blocking layer 6.

[0092]Therefore, it is required for electron injection efficiency from the negative pole 8 to be a compound which can convey efficiently an electron which has high electron mobility and was poured in highly as an electron-transport-property compound used for the electron transport layer 7.

[0093]As a material which fulfills such conditions, metal complexes, such as an aluminium complex of 8-hydroxyquinoline (JP,59-194393,A), A metal complex of 10-hydroxybenzo[h] quinoline, an oxadiazole derivative, A distyrylbiphenyl derivative, a silole derivative, 3-, or 5-hydroxyflavone metal complex, A benzoxazole metal complex, a benzothiazole metal complex, tris benzimidazolyl benzene (U.S. Pat. No. 5,645,948), A quinoxaline compound (JP,6-207169,A), a phenanthroline derivative (JP,5-331459,A), 2-t-butyl-9,10-N,N'-dicyanoanthraquinonediimine, n type hydrogenation amorphous carbonization silicon, n type zinc sulfide, n type zinc selenide, etc. are mentioned.

[0094]5-200 nm of thickness of the electron transport layer 6 is usually 10 - 100 nm preferably.

[0095]The electron transport layer 7 is formed by laminating on the electron hole transporting

bed 6 with the applying method or a vacuum deposition method like the electron hole transporting bed 4. Usually, a vacuum deposition method is used.

[0096]The raising efficiency of a hole injection further and making adhesion force to the anode 2 of the whole organic layer improve purpose, as shown in drawing 3, inserting the anode buffer layer 3 between the electron hole transporting bed 4 and the anode 2 is also performed. By inserting the anode buffer layer 3, an effect that a power surge when the continuation drive of the element is carried out by constant current is also controlled is acquired at the same time driver voltage of an early element lowers. As conditions required of material used for the anode buffer layer 3, A thin film with it can be formed, it is mentioned that stability, i.e., the melting point, and glass transition temperature are thermally high, and it is as the melting point. As not less than 300 ** and glass transition temperature Not less than 100 ** is preferred. [good contact to the anode 2 and] [uniform] It is mentioned that ionization potential is low and a hole injection from the anode 2 is easy and that hole mobility is large.

[0097]Until now for this purpose Phthalocyanine compounds, such as a copper phthalocyanine (JP,63-295695,A), Poly aniline (Appl. Phys. Lett., 64 volumes, 1245 pages, 1994), a polythiophene (Optical Materials -- 125 pages nine volumes) organic compounds in 1998 etc., and a weld slag carbon film (Synth. Met. -- 91 volumes) Metallic oxides (J. Phys. D, 29 volumes, 2750 pages, 1996), such as 73 pages, 1997, a vanadium oxide, a ruthenium oxidation thing, a molybdenum oxide, are reported.

[0098]Although thin film forming is possible also for the anode buffer layer 3 like the electron hole transporting bed 4, when it is an inorganic substance, a sputtering technique, electron beam evaporation method, and plasma CVD method are used further.

[0099]thickness of the anode buffer layer 3 formed as mentioned above -- usually -- 3-100 nm -- desirable -- It is 5-50 nm.

[0100]To an interface with the negative pole 8, the luminous layer 5, or the electron transport layer 7, LiF, Inserting ultra-thin insulator layers (0.1-5 nm of thickness), such as MgF_2 and Li_2O, It is the effective method of raising the efficiency of element (Appl. Phys. Lett., 70 volumes, 152 pages, 1997; JP,10-74586,A;IEEETrans. Electron. DeVices, 44 volumes, 1245 pages, 1997).

[0101]It is also possible to laminate on a structure contrary to drawing 1, i.e., a substrate, in order of the negative pole 8, the hole blocking layer 6, the luminous layer 5, the electron hole transporting bed 4, and the anode 2, and at least one side is able to provide organic electroluminescence devices of this invention between two substrates with high transparency, as mentioned already. It is also possible similarly to laminate in a structure contrary to said class composition shown in drawing 2 and drawing 3. It may have arbitrary layers between the anode or the negative pole, and a luminous layer besides each class shown in drawing 1, drawing 2, and drawing 3.

[0102]Also in any of structure where a single element, an element which consists of structure where it has been arranged at array form, the anode, and the negative pole have been arranged in the shape of an X-Y matrix, organic electroluminescence devices can apply this invention.

[0103]According to the organic electroluminescence devices of this invention, an element of high luminous efficiency with which color purity has been improved [in / it is good and / driving stability] greatly is obtained by making a hole blocking layer contain a compound which has specific N-phenyl carbazole skeleton. According to this invention, full color or performance outstanding in application to a panel of multicolor can be demonstrated from an element which was excellent in stability with a conventionally difficult blue light element especially being obtained.

[0104]

[Example]Next, although an example explains this invention still more concretely, this invention is not limited to the statement of the following examples, unless the gist is exceeded.

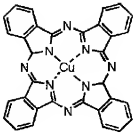
[0105]The organic electroluminescence devices which have the structure shown in example 1 drawing 3 were produced by the following methods.

[0106]It is an indium-tin-oxide (ITO) transparent conducting film on the glass substrate 1. The usual photolithography technique and chloride etching are used for what was deposited 150 nm (Geomatec make; electron beam membrane formation article; 15ohms of sheet resistance). It patterns after the stripe of 2-mm width. The anode 2 was formed. The ITO board which carried out pattern formation was dried by the nitrogen blow after washing in order of ultrasonic cleaning by acetone, rinsing by pure water, and ultrasonic cleaning by isopropyl alcohol, finally the ultraviolet-rays ozone wash was performed, and it installed in the vacuum evaporator. It exhausted using the oil diffusion pump provided with the liquid nitrogen trap after the oil sealed rotary pump performed rough exhaust air of the above-mentioned device until the degree of vacuum in a device became below $2x10^{-6}$Torr (about $2.7x10^{-4}$Pa).

[0107]Subsequently, the copper phthalocyanine (a crystal form is beta type) shown in the following put into the molybdenum boat arranged in the above-mentioned device is heated, It vapor-deposited with degree-of-vacuum $1.7x10^{-6}$Torr (about $2.3x10^{-4}$Pa) and the evaporation rate of 0.14nm/second, and the anode buffer layer 3 of 10 nm of thickness was formed.

[0108]

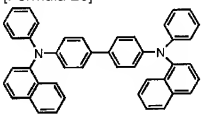
[Formula 27]



[0109]Next, it vapor-deposited by heating the 4,4'-bis[N-(1-naphthyl)-N-phenylamino] biphenyl which was put into the ceramic crucible arranged in the above-mentioned device and which is shown below with the tantalum wire heater around a crucible. The temperature of the crucible at this time was controlled in 245-260 **. Degree-of-vacuum 1.3x10 $^{-6}$Torr at the time of vacuum evaporation (about 1.7x10 $^{-4}$Pa) and an evaporation rate formed the electron hole transporting bed 4 of 60 nm of thickness in a second in 0.24nm /.

[0110]

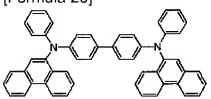
[Formula 28]



[0111]Then, the triphenylamine derivative (EM-1) of a structural formula and the coumarin derivative (DYE-1) of a blue fluorochrome which are shown below were made into above-mentioned Mr. electron hole transporting bed 4 top **** as a material of the luminous layer 5, and vapor codeposition was performed at a rate of 100:1. The temperature of the crucible at this time was controlled in 275-295 ** and 193-198 **, respectively. The evaporation rate of 1.1x10 $^{-6}$Torr (about 1.5x10 $^{-4}$Pa) and EM-1 is 0.20nm/second, and the degree of vacuum at the time of vacuum evaporation formed the luminous layer 5 of 30 nm of thickness. The ionization potential determined using the Riken Keiki bottom photoelectron spectroscopy device of the atmosphere (AC-1) (host compound of the luminous layer (EM-1) 5) was 5.22 eV. Hereafter, each ionization potential in this application example is the value determined similarly.

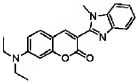
[0112]

[Formula 29]



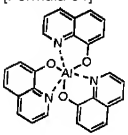
(EM-1)

[0113]
[Formula 30]



(DYE-1)

[0114]The illustration compound (H-6) was laminated by 10-nm thickness with the evaporation rate of 0.12nm/second as the hole blocking layer 6. The degree of vacuum at the time of vacuum evaporation was 1.1×10^{-6}Torr (about 1.5×10^{-4}Pa). The ionization potential of the illustration compound (H-6) similarly determined as the host compound of the luminous layer 5 was 5.96 eV.
[0115]Subsequently, the 8-hydroxyquinoline complex of the aluminum shown in the following structural formulae as the electron transport layer 7 and aluminum$(C_9H_6NO)_3$ were similarly vapor-deposited on the hole blocking layer 6. The crucible temperature of the 8-hydroxyquinoline complex of aluminum at this time was controlled in 295-305 **, the degree of vacuum at the time of vacuum evaporation was set to 8.0×10^{-7}Torr (about 1.1×10^{-4}Pa), and thickness was 35 nm in evaporation rate in a second in 0.24nm /.
[0116]
[Formula 31]



[0117]When carrying out vacuum deposition of above-mentioned electron hole transporting bed 4, luminous layer 5, hole blocking layer 6, and electron transport layer 7, substrate temperature was held to the room temperature.
[0118]The element which performed vacuum evaporation to the electron transport layer 7 is once taken out from the inside of said vacuum evaporator in the atmosphere here, As the mask for negative pole vacuum evaporation The stripe shape shadow mask of 2-mm width, It was made to stick to an element so that it may intersect perpendicularly with the ITO stripe of the anode 2, and it exhausted until it installed in another vacuum evaporator and the degree of vacuum in a device became below 2.2×10^{-6}Torr (about 3.0×10^{-4}Pa) like the time of formation

of an organic layer.

[0119]Then, lithium fluoride (LiF) was first formed on the electron transport layer 7 by 0.5 nm of thickness by evaporation rate [of 0.04nm/second], and degree-of-vacuum 4.1x10 $^{-6}$Torr (about 5.5x10 $^{-4}$Pa), using a molybdenum boat as the negative pole 8. Next, aluminum was similarly heated by the molybdenum boat, the aluminum layer of 100 nm of thickness was formed by evaporation rate [of 0.41nm/second], and degree-of-vacuum 9.0x10 $^{-6}$Torr (about 1.2x10 $^{-3}$Pa), and the negative pole 8 was completed. The substrate temperature at the time of vacuum evaporation of the above two-layer type negative pole 8 was held to the room temperature.

[0120]The organic electroluminescence devices which have an emission area portion with a size of 2 mm x 2 mm as mentioned above were obtained. The luminescent characteristic of this element is shown in Table 1. In Table 1, it is luminous efficiency. The value in 100 cd/m^2, and luminosity/current are voltage about inclination of a luminosity-current density characteristic. The value in 100 cd/m^2 is shown respectively. Stability was evaluated from the ratio of initial luminance and the luminosity of 60 seconds after, when DC drive was carried out by current density 0.25 A/cm^2. Or more for 0.98, the luminance ratio (luminosity/initial luminance of 60 seconds after) made "fitness" "it excels" and less than [0.90 or more] 0.98, and presupposed "It is inferior of less than 0.90."

[0121]Maximum wavelength of the emission spectrum of an element It is 473 nm and was identified the thing from a fluorochrome (DYE-1). There is almost no brightness degradation and it excels in stability.

[0122]Comparative example 1 hole blocking layer was not provided, but the thickness of the electron transport layer was 45 nm, and also the element was produced like Example 1. In this element, the ionization potential of aluminum$(C_9H_6NO)_3$ which forms the electron transport layer 7 which is in contact with the luminous layer instead of the hole blocking layer 6 was 5.41 eV. The luminescent characteristic of this element is shown in Table 1.

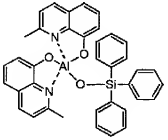
[0123]Maximum wavelength of the emission spectrum of an element At 514 nm, the target blue light was not obtained but the green emission from the 8-hydroxyquinoline complex of aluminum used as an electron transport layer was observed.

[0124]8-HIDORIKISHI quinoline complex (ionization potential: 5.51 eV) of the silanol aluminum shown in the following structural formulae was used as comparative example 2 hole blocking layer, and also the element was produced like Example 1. The luminescent characteristic of this element is shown in Table 1.

[0125]Maximum wavelength of the emission spectrum of an element Although the target blue light was obtained at 473 nm, brightness degradation is large and lacks in driving stability.

[0126]

[Formula 32]

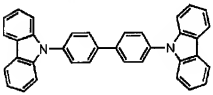


[0127]The 4,4'-N,N'-dicarbazolyl biphenyl (ionization potential: 5.93 eV) shown in the following structural formulae was used as comparative example 3 hole blocking layer, and also the element was produced like Example 1. The luminescent characteristic of this element is shown in Table 1.

[0128]Maximum wavelength of the emission spectrum of an element At 524 nm, the target blue light was not obtained but the green emission from the 8-hydroxyquinoline complex of aluminum used as an electron transport layer was observed.

[0129]

[Formula 33]



[0130]The illustration compound (H-25) was used as example 2 hole blocking layer, and also the element was produced like Example 1. The luminescent characteristic of this element is shown in Table 1.

[0131]Maximum wavelength of the emission spectrum of an element The target blue light was obtained at 471 nm, there is also little brightness degradation and driving stability was good.

[0132]

[Table 1]

	発光色	最大発光輝度 [cd/m²] @0.25A/cm²	発光効率 [lm/W] @100cd/m²	輝度／電流 [cd/A]	電圧 [V] @100cd/m²	安定性
実施例1	緑青	4500	1.3	2.0	5.0	優れる
比較例1	黄緑	4900	1.2	2.1	5.4	良好
比較例2	緑青	4900	1.5	2.6	5.5	劣る
比較例3	黄緑	2900	0.8	1.4	5.1	良好
実施例2	緑青	3300	0.8	1.5	6.0	良好

[0133]

[Effect of the Invention]According to the organic electroluminescence devices of this invention, it is possible to obtain only luminescence from the luminescent material selected arbitrarily, and luminescence which was further excellent in driving stability can obtain as explained in full detail above. An improvement of the driving stability of the conventionally especially difficult blue light element is remarkable.

[0134]The organic electroluminescence devices by this invention Therefore, a flat panel display (for example, the object for OA computers and a flat TV), The application to the light source (for example, the light source of a copying machine, the back light source of a liquid crystal display or instruments), the plotting board, and the beacon light which employed the feature as a mounted display device, and a cellular-phone display and a surface light object efficiently can be considered, and the technical value is large.

[Translation done.]